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GROWTH OF BULK WIDE BANDGAP SEMICONDUCTOR CRYSTALS AND THEIR POTENTIAL APPLICATIONS

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Abstract

Developments in bulk crystal growth research for electo-optical devices in the Center for Photonic Materials and Devices since its establishment have been reviewed. Purification processes and single crystal growth systems employing physical vapor transport and Bridgman methods were assembled and used to produce high purity and superior quality wide bandgap materials such as heavy metal halides and II-VI compound semiconductors. Comprehensive material characterization techniques have been employed to reveal the optical, electrical and thermodynamic properties of crystals, and the results were used to establish improved material processing procedures. Post-growth treatments such as passivation, oxidation, chemical etching and metal contacting during the X-ray and gamma-ray device fabrication process have also been investigated and low noise threshold with improved energy resolution has been achieved.

I. Introduction

Over the last decades semiconducting compound materials have been recognized and developed for various electro-optical devices applications. Among them, wide bandgap 1 I-VI compound semiconductors have attracted extensive interest and research efforts due to their potential uses as room temperature X-ray and gamma ray detectors[1-7], IR detectors light-emitting devices (LED) in the visible range[9], tunable solid state laser[10], optical limiting and optical communication devices, etc. One of the most essential steps in the the development of a device is the crystal growth process itself. The ability to produce structurally and chemically pure crystals plays a vital role in the development of the practical device, and currently is also an important subject of NASA microgravity materials research program. The growth of single crystals and materials processing under micro gravity environment can prevent gravitational-induced effects, and produce more homogeneous composition and stress-free materials. Materials characterization techniques are also important in providing basic electrical and defect information, and they can be correlated to the starting material and initial crystal growth process in order to optimize the purification and growth conditions. The actual device can then be fabricated and tested to evaluate its performance and potential for practical applications. The Materials Science and Application Group (MSAG) in the Fisk University Center for Photonic Materials and Devices (CPMD) has investigated the fabrication and evaluation of radiation detectors based on wide bandgap II-VI compound semiconductors and heavy metal halides. These materials not onl y have great potential in medical, industrial and environmental applications, but also in space exploration, as X-ray and gamma ray spectrometers and imaging arrays. In this paper we report recent developments in materials processing and characterization and device fabrication.

II. Material Purification and Crystal Growth

Typically, starting materials which may purchased from commercial vendors with nominal purity of 99.9999% or synthesized from pure elements by stoichiometric weight, need to be further purified and/or adjusted to stoichiometric composition before crystal growth and device fabrication. In our laboratory, zone-refining and vacuum sublimation are two standard processes to achieve this goal. Zone-refining was first introduced in 1952 [11], and has been successfully implemented by us to purify elements, such as Se and Te, and heavy metal halides, such as HgI_2, PbI_2 and BiI_3. The characteristic effect of zone-refining is to accumulate impurities at the ends of an ingot, thus leaving pure material in the central section. Figure "1 shows the distribution of impurity concentrations of Mg, Ag, Cu and Cr along a zone-refined ingot of HgI_2[12].

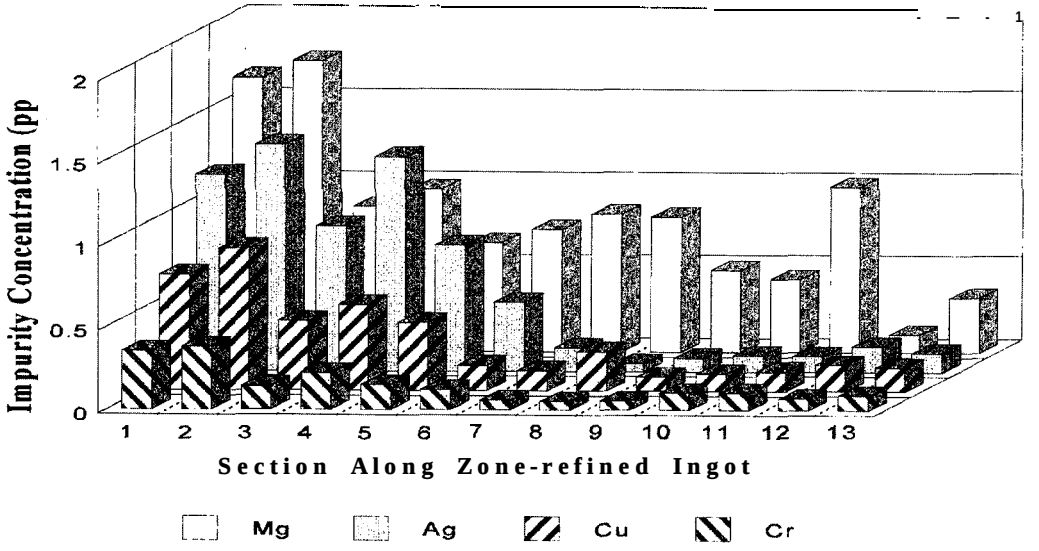
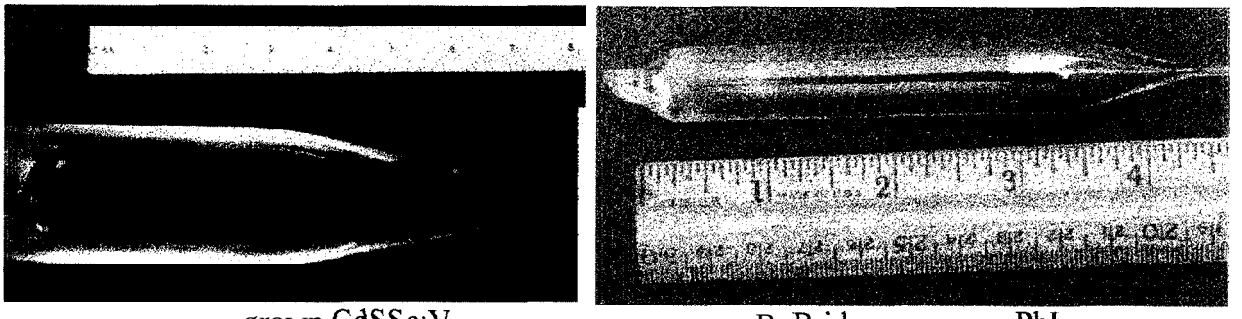


Figure 1. Impurity concentration distribution along zone-refined HgI_2.

In this particular case it is clear that most impurities accumulated at one end (1-4) leaving the other section to be the purest part of the ingot. A similar purification effect has been observed for PbI_2[13]. Vacuum sublimation is a routine method used in our laboratory to purify starting materials from impurities having higher (under dynamic vacuum) or lower (closed tube) vapor pressures. Especially, baking the starting material under a dynamic pumping before sealing off the crystal growth ampoule plays an important role in correcting the deviation from stoichiometry of the material.

Two crystal growth methods frequently used in our laboratory are Physical Vapor Transport (PVT) and Bridgman methods. PVT method is the crystal growth under vapor - solid equilibrium conditions. The temperature of the starting material (powder form) is higher than the nucleation/crystal growth region. This imposed temperature gradient leads to a diffusive-convective flow resulting in a net mass transport of vapor species towards the crystal growth site. The vapor species may consist of molecules of the material itself, such as $PbI_2(solid) \rightarrow PbI_2(vapor)$, or dissociated into its separate constituents, such as CdTe (solid) $\rightarrow$ $Cd(vapor) + \frac{1}{2} Te_2$ (vapor), and residual gases. The reverse process occurs when vapor species nucleate and then continue to condense on the crystal growth interface at a rate of 3-5 mm/day. A typical PVT grown vanadium doped CdSSe single crystal is shown in Figure 2A, currently being investigated for its photorefractive effect and optical limiting properties. Other semiconductor systems, such as HgI_2, H-VI binary and ternary sulfides, selenides and tellurides were also successfully grown from PVT frequently in our laboratory.



grown CdSSe:V

B. Bridgman grown PbI_2

Figure 2. As-grown single crystals in their growth ampoule.

The Bridgman growth method is basically a controlled freezing process taking place under liquid - solid equilibrium conditions. The growth also takes place under a temperature gradient, and the mechanism is to produce a single nucleus from which a single crystal will propagate and grow. This is achieved by allowing the solid - liquid interface to move slowly (5-50 mm/day) until the whole molten charge is solidified. A PbI_2 single crystal is shown in Figure 2B. Compared to other growth methods, Bridgman method is considered to be a rather simple crystal growth method, but several limitations still exist. The Bridgman method can not be applied to a material system which decomposes before it melts, systems having components with high vapor pressure, and materials exhibiting destructive solid - solid phase transformations which will compromise the crystalline quality on cooling the crystal at the end of the growth run. HgI_2 is a typical a material which is not suitable for Bridgman growth. It has high vapor pressure and undergoes a solid - solid phase transition from $\alpha \rightarrow \beta$ at 130 °C before its melting temperature at 258 "C. Therefore HgI_2 can only be grown only by PVT, while PbI_2, lacking such a phase transition can also be grown by Bridgman method.

III. Materials Characterization

Several characterization methods based on spectroscopes, microcopies and thermal analysis techniques have also been employed to investigate and reveal the optical, electrical, structural and thermodynamic properties of the grown crystals.

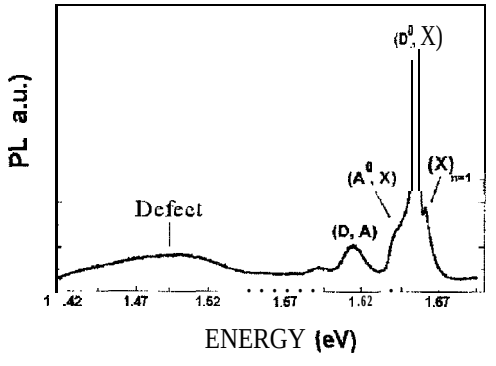


Figure 3. Low temperature photoluminescence spectrum of $Cd_{0.9}Zn_{0.1}Te$.

A. Spectroscopic Characterization - Low temperature (11 K) photoluminescence, x-ray photoelectron spectroscopy (XPS), UV-Vis, infrared spectroscopy (JR) are frequently used, helpful techniques which reveal information of both bulk and surface electronic and optical properties of material. Figure 3 shows a low temperature (11 K) photoluminescence spectrum of C $d_{0.9}Zn_{0.1}Te$ etched by 5% bromine in methanol and 2% bromine-20% lactic acid in ethylene glycol[14]. The spectrum reveals that the etched surface has a stoichiometric composition and superior structure as evidenced by the appearance of a free exciton in the ground state, $(X)_{n=1}$ and the large $I(D^o,X)/I_{defect}$ (I_{defect} is the broad peak center around 1.5 eV) ratio. Such information is important in understanding surface modifications of a material, and directly relates to the device performance. XPS is a chemical analysis technique which can revealed the composition and chemical species on the surface of materials. Figure 4 shows the XPS spectra of Te 3d peaks of $Cd_{0.9}Zn_{0.1}Te$ etched by H_2O_2[15]. The spectra revealed that H_2O_2 did form a oxide layer on the crystal surface consisting of TeO_2 , the oxidation increasing with H_2O_2 etching time. After a 15 min treatment, the oxide layer thickness could be estimated to be 20-30 Å, based on the relative intensity of Te and TeO_2 peaks. This information is particularly important in the device fabrication since it was found by us to lower the electronic noise of radiation detectors.

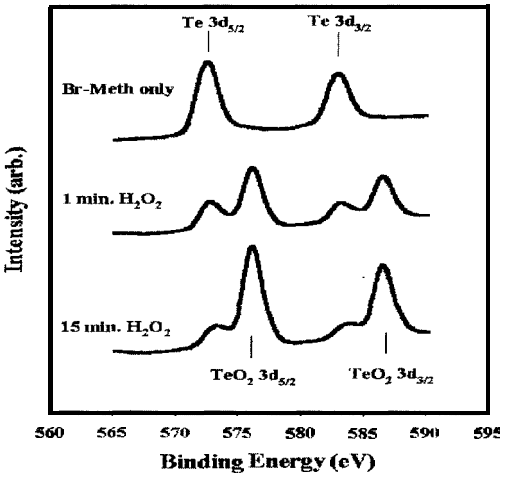


Figure 4. XPS spectra of Te and TeO_2 of H_2O_2 etched $Cd_{0.9}Zn_{0.1}Te$.

B. Microscopic Characterization - Surface morphology can be revealed directly from optical microscopy and high resolution atomic force microscopy (AFM). The morphology of as-grown and

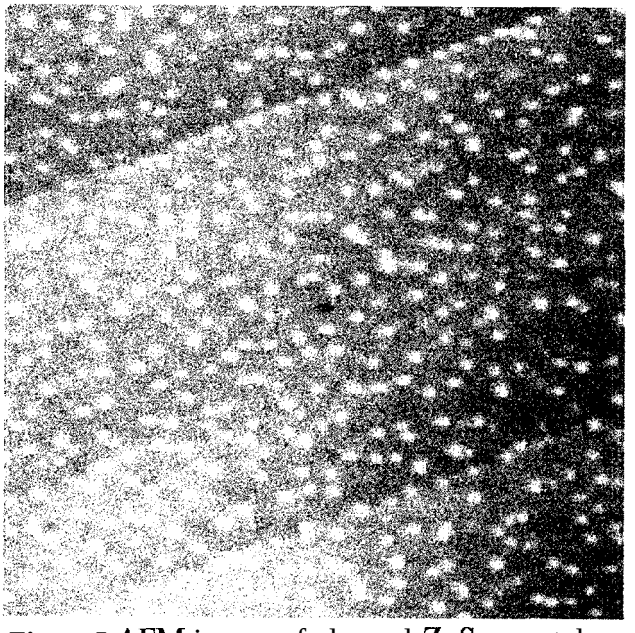


Figure 5 AFM image of cleaved ZnSe crystal, scan size is 500 X 500 nm

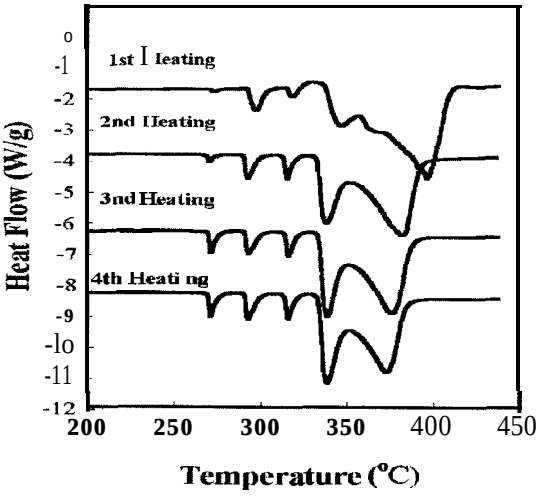


Figure 6. DSC thermograms of Bridgman grown BiI_3.

cleaved crystal surfaces can give important information related to the initial purification process and crystal growth conditions. Figure 5 shows an AFM image of a cleaved ZnSe crystal. This image revealed that second phase precipitation has occurred and that the concentration of precipitates is higher along low angle (approx. 0.1 ° tilt) grain boundaries. The density of precipitates is calculated to be about 1013 m^{-2} with 20 nm as an upper limit of the size of precipitate s. Using existing phase diagrams, these precipitates have been identified by differential scanning calorimetry (DSC) as a Se-rich second phase existing in ZnSe solid solution. This result was correlated to the initial purification process and crystal growth conditions, and used to improve the growth process of ZnSe crystals with near-stoichiometric composition,

C. Thermal Analysis - Differential scanning calorimetry (DSC), thermomechanical analysis (TMA) and themogravimetric analysis (TGA) have been employed for characterization of mechanical and thermodynamic properties such as phase transitions and melting temperatures, heat of fusion and impurity analysis of materials. Figure 6 shows the DSC thermograms of a Bridgman grown BiI_3 crystal. While the melting temperature for stoichiometric BiI_3 is 408 °C , the Bridgman grown crystals show a depression of melting temperature and some second phases toward low temperature during the first heating run. These second phases were more developed during the second, third and fourth heating cycles, and at the same time the melting temperature has been depressed even more. These second phases were identified from temperature-composition phase diagrams as Bi-rich phases coexisting in a BiI_3 solid solution. PVT grown BiI_3 was also investigated by DSC, not shown here, and the thermograms showed no second phase with a melting temperature near 408 "C. These DSC results clearly show that PVT is the most suitable method for crystal growth of BiI_3 and the melting process produced Bi-rich second phases.

IV. **Device Fabrication and Evaluation**

Room temperature radiation detectors have been fabricated and tested in terms of resistivity and photoresponse. A typical wafer size for radiation detector is about 10×10×2 mm. After wafers are cut from the as-grown crystal, they are mechanically polished, chemically etching to remove surface damage layers and metal electric contacts are applied. Additional surface treatments such as passivation and oxidation are also employed. Each fabrication step may affect the detector performance and therefore unwanted surface effects, such as deviation from stoichiometry, microscopic damage and creation of charge carrier traps, are of great concern. Figure 7 shows the results from current -voltage measurements on the same $Cd_{0.9}Zn_{0.1}Te$ waffer, etched by various etchants[14]. The triangle curve which shows data for the same treatment as in Figure 3, illustrated the most linear ohmicity and the lowest surface leakage current, 5 times lower than other etchants (diamonds: 5% bromine in methanol; circles: 2°/0 bromine plus 20% lactic acid in ethylene glycol.

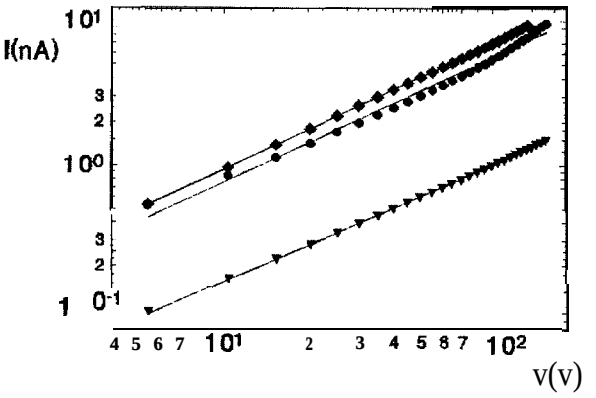


Figure 7. Comparison of I-V curves of $Cd_{0.9}Zn_{0.1}Te$ detector treated by different etchant s.

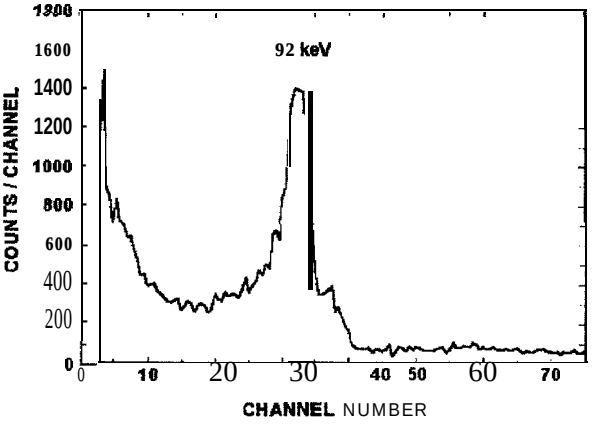


Figure 8. ^{133}Ba spectrum of $Cd_{0.9}Zn_{0.1}Te$.

The good surface quality revealed by the PL spectrum correlates directly to the I-V results in Figure 7. The improvement in the surface leakage current leads to a reduction of the noise threshold allowing for a better low energy x- and gamma-ray spectral response. Figure 8 shows the radiation spectrum obtained from the same sample as in Figures 3 and 7. The noise threshold is the lowest compared to spectra fromsamples treated with the other two etchants, allowing a good energy resolution of 12% of Full-Width-at-Half-Maximum (FWHM) for the 32 keV energy line.

V. Summary

Wide bandgap semiconductor single crystals, such as heavy metal halides and II-W compounds, have been grown by physical vapor transport and Bridgman methods. Zone-refining and vacuum sublimation techniques were used to purify and adjust the stoichiometric composition of the starting material, and were proven to be effective. Several spectroscopic, microscopic and thermodynamic analytical techniques were employed to investigate the optical, electrical and structural properties of crystals. These results revealed information regarding micro- and macroscopic defects, impurities and modifications resulting from source material, growth process, post-growth treatment and device fabrication. Crystal growth and processing conditions have been correlated with this information and were optimized to achieve the purest and highest quality materials for practical device applications. Room temperature x- and gamma-ray detector have been developed and their performance in terms of surface leakage current evaluated and improved. Surface passivation, chemical etching and metal contacting are currently under investigation to further improve device performance, Future works will involve optimization of material purification and crystal growth processes to produce high purity and low defect crystals, development of sensitive material characterization tools allowing a better understanding of defects formation and their correlation with processing conditions.

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